Chapter 3

Biogenic carbon fraction of biogas and natural gas fuel mixtures determined with ^{14}C

Abstract

This study investigates the accuracy of the ^{14}C-based calculation of the biogenic carbon fraction for different biogas samples and bio-fossil gas mixtures. The focus is on the uncertainty in the ^{14}C reference values for 100% biogenic carbon and on the ^{13}C-based isotope fractionation correction of the measured ^{14}C values. The separately (AMS) measured CO_2 and CH_4 fractions of 8 different biogas samples showed ^{14}C values between 102 and 116 % (pmC). The $\delta^{13}C$ values of these samples varied between -6 and +31 ‰ for the CO_2 fraction and between -28 and -62 ‰ for the CH_4 fraction. The uncertainty in calculated biogenic carbon fractions due to uncertainty in the ^{14}C reference values depends on the available information about the origin of the used biogenic materials. It varies between ± 0.5 and ± 3.5% (absolute) depending on the type of biogas. A method is proposed to minimize this kind of uncertainty for different groups of biogases. The calculated biogenic carbon fraction deviates up to ± 2.5% for bio-fossil gas mixtures, if the applied isotope fractionation correction is based on the $\delta^{13}C$ value of the mixed bio-fossil sample instead of the biogenic $\delta^{13}C$ value. Combination of both error-sources shows that the uncertainty in the calculated biogenic carbon fraction varies between ± 0.7% and ± 4.5%, depending on the type of biogas in the sample.

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3.1 Introduction

The use of biogas, specifically its biomethane fraction, as an alternative for natural gas increases due to more demand and an increasing number of (agricultural) biogas production plants. Although biogas is currently mainly used in combination with heat and power stations (CHP; production of electricity at the biogas production site), biogas is increasingly used as vehicle fuel and injected into local and national gas grids (Weiland 2010). Hence, there is an upcoming market in which biogas is combusted alone or as part of biogenic/fossil fuel mixtures. Verification of the biogenic carbon composition of produced bio-methane, bio-fossil gas mixtures and of related CO_2 emissions, using preferably the ^{14}C method, becomes more relevant. So far, however, the ^{14}C method was only investigated and tested for different liquid and solid fuels and for flue gas CO_2 (Dijs et al. 2006; Staber et al. 2008; Mohn et al. 2008; Palstra and Meijer 2010). The ^{14}C method was not demonstrated yet for fuel mixtures containing biogas and natural gas.

This chapter will discuss to what extent two different aspects within the ^{14}C-method introduce (systematic) errors in the calculated biogenic carbon fraction (in short: bioC fraction) when applied to fuel mixtures containing biogas and natural gas. One of the investigated aspects is the uncertainty in the ^{14}C reference value for 100% biogas carbon (its methane fraction in particular). To calculate the bioC fraction of a sample, the ^{14}C value of this sample needs to be compared with the ^{14}C value of the bioC fraction of the sample (reference value, $^{14}C_{bio}$). As explained in chapter 1, the ^{14}C value of biogenic carbon is in general determined by the ^{14}C value of the atmospheric CO_2 during the time period of photosynthesis by plant material and shows large temporal and spatial variations. Especially when biogas itself needs to be verified on its 100% bioC content or when biogas and fossil gas are already mixed, $^{14}C_{bio}$ in these kinds of samples cannot be determined based on direct ^{14}C measurement of the sample itself, but needs to be approximated based on (most likely) atmospheric $^{14}CO_2$ values. This approximation introduces an uncertainty in the calculated bioC fraction, which increases when less information is available about the composition and origin (average harvest year) of the bioC material in the investigated sample. It is shown in this study for eight different biogas samples from different production sites. In the applied approach the investigated biogas samples were divided into four different 'biotype' groups with each a certain approximated ^{14}C reference value and an accompanying uncertainty, merely based on the expected harvest year of the biogenic materials that were used in the specific biogas production processes.

Another aspect that was investigated in this study, and which has not been investigated so far for any kind of bio-fossil fuel mixtures, is isotope fractionation correction of measured ^{14}C values. This aspect within the ^{14}C method can cause systematic errors in the calculated bioC fraction if not applied well. To compare the measured ^{14}C

value of a sample with $^{14}C_{bio}$, both ^{14}C values should be calculated according to the same specific standardized calculations. ^{13}C-based isotope fractionation correction (to a normalized value) should be part of these calculations, especially if the biogenic carbon sources of the measured sample and the ^{14}C reference value are different and have different $\delta^{13}C$ values. Norton & Devlin (2006) have shown examples of deviations in the calculated bioC fraction if the isotope fractionation correction has only been applied to the ^{14}C reference value but not to the measured ^{14}C value of the sample itself.

When applied, the isotope fractionation correction should in principle only correct for isotope fractionation that has occurred in the ^{14}C containing carbon source. Hence, for ^{14}C applications in which mixtures of fossil and biogenic carbon are analyzed, the isotope fractionation correction should only correct for isotope fractionation that has occurred in the bioC fraction (until measurement). It is, however, often not possible to investigate the $\delta^{13}C$ values of the bioC and fossilC fractions separately. In general only the $\delta^{13}C$ value of the final mixture will be analyzed, including the contribution of the fossil carbon. Mook (1980) has described this ^{13}C "mixing effect" on the isotope fractionation correction for atmospheric CO_2 samples. De Rooij et al. (2008) present a calculation study for (modern) carbon AMS samples diluted with fossil carbon before graphitization. The ^{13}C-mixing effect on the isotope fractionation correction has not been investigated yet for different fuels and flue gas CO_2 samples. This effect will in general not be relevant in case the biogenic carbon and fossil carbon have very similar $\delta^{13}C$ values (like wood and coal) and the fraction of fossil carbon is relatively small. Natural gas and biogas (their methane fractions), however, both show a large variation in $\delta^{13}C$ values, with values ranging between -25 and -80 ‰ (Levin et al. 1993; Bergamaschi et al. 1998; Milkov 2005; Laukenmann et al. 2010). Gas fuel mixtures containing biogas and/or natural gas might therefore show significant ^{13}C mixing effects on the isotope fractionation correction, as the measured $\delta^{13}C$ value of the bio-fossil mixture can be very different from the $\delta^{13}C$ value of the bioC fraction in the sample. Hence, for these kinds of mixtures some systematic deviation in the ^{14}C-based bioC fraction can be expected. This study quantifies these deviations, both theoretically and experimentally, for different biogas and natural gas fuel mixtures. The necessary calculations will be presented in detail and the results are tested and illustrated with actual biogas/natural gas mixtures. Finally, this chapter will show how both investigated aspects together affect the accuracy of the ^{14}C method for biogas/natural gas mixtures.

This chapter is very similar to the published research paper (Palstra and Meijer, 2014). Some (introduction) parts are moved to chapter 1. The research was part of project A2 'Agate-1' of the green gas project EDGaR (Energy Delta Gas Research).

3.2 Experimental methods

To determine the ^{14}C values of biogas from different production plants and to investigate the isotope fractionation correction of bio-fossil gas mixtures, different biogas and natural gas samples were acquired, pre-treated and then combusted to pure CO_2. The $\delta^{13}C$ value of this CO_2 was analyzed by isotope ratio mass spectrometry (IRMS) and, after graphitization, its ^{14}C value by AMS. To investigate the isotope fractionation correction, two different mixture series of biogenic and fossil CO_2 (both from combusted CH_4 samples) were made: one from biogenic and fossil CO_2 with very different $\delta^{13}C$ values and one from biogenic and fossil CO_2 with similar $\delta^{13}C$ values. For every pair of biogenic and fossil CO_2 at least five different CO_2 mixtures with bioC fractions between 0 and 100% were made and analyzed on $\delta^{13}C$ and ^{14}C.

3.2.1 Biogas and natural gas samples

Eight raw biogas samples and three natural gas samples were obtained in 2011 from DNV KEMA (since 2013: DNV GL), Groningen, the Netherlands. DNV KEMA sampled the gases at production sites (except "Groningen gas", which was sampled in the laboratory of KEMA itself) and determined the composition of the gases based on gas chromatography (GC) analysis in their laboratory. The gas was sampled with 3-L gasbags of various types (SKC Tedlar bags with polypropylene fitting, SKC Flex Foil bags with polypropylene fitting and Tedlar bags from BaSystemen with polypropylene fitting).

3.2.2 Gas sample pretreatment

Before the gas samples were combusted to CO_2, all samples were pretreated. Part of the pretreatment of the biogas samples was different to that of the natural gas samples, due to the larger CO_2 fraction present in the (raw) biogas samples compared to the natural gas samples. The investigated raw biogas samples contained 8 - 42% CO_2 (mol. fraction), while the natural gas samples contained maximal 1 - 3% CO_2. In this study the CO_2 fraction in the biogas samples were separated from the CH_4-fraction (and some minor other components), to gain insight in the isotopic carbon composition of both carbon components separately. As the removal of the CO_2-fraction is common practice in the pre-treatment of biogas to obtain a safe, energy-efficient, and reliable energy source (biomethane or what is often called "green gas"), the isotope measurement results of the combusted CH_4-fraction are also a realistic example of carbon isotope results that can be expected if pre-treated biogas samples are combusted.

In this study 360 - 490 mL of raw biogas was prepared, delivering 250-300 mL CO_2 after combustion of the CH_4-fraction. This amount of CO_2 was necessary because it formed the basis of our investigated biogas-natural gas mixtures. To separate the CO_2 and CH_4 fractions of a raw biogas sample, the sample was introduced in a vacuum-pumped system,

water and heavy molecules were cryogenically trapped with dry ice/ethanol (-78ºC) and the CO_2 was cryogenically trapped in an iso-pentane trap (-160 ºC). The remaining CH_4-fraction was cryogenically trapped with liquid N_2 (-196 ºC) in a 20-mL flask that contained approximately 4 g of molecular sieve 5A. The trapped CO_2-fraction was transferred to a cylinder. To obtain sufficient CH_4 for the combustion process, the CO_2-CH_4 separation procedure was performed twice due to size limitations of the system. The absorbed CH_4-fraction in the 20-mL flask was desorbed from the molecular sieve material (by heating it) while connected to a vacuum-pumped 2.5-L flask. The obtained gas sample in the 2.5-L flask was diluted with pure N_2 gas to 1 atm. to make it suitable for the combustion system and to obtain a low methane concentration (to enhance the combustion efficiency in the specific combustion system at a certain gas flow rate). The CH_4-fraction of the biogas sample was then ready to be combusted.

For natural gas samples, the procedure prior to combustion was slightly different, as the separation of CO_2 was not necessary. Only water (if present) and heavy molecules were removed from the natural gas samples by trapping them cryogenically in a vacuum-pumped system with a dry ice/ethanol mixture. Approximately 380 mL of gas was transferred to a 2.5-L flask and, similar to the biogas samples, this flask was filled to 1 atm. with pure nitrogen gas as well.

3.2.3 Gas sample combustion

The combustion method and the procedure to obtain pure CO_2 was the same for biogas and natural gas samples. After the pre-treatment, the 2.5-L flask with gas sample was connected in series with a (pure) nitrogen gas flow (≈ 35 mL/min). This flow passed through the flask and then, together with the gas sample, through the entire combustion system. The gas flow (of gas sample + N_2) first passed a volume that was oven-heated to 1000 ºC. At the end of this heated volume, an O_2 flow was introduced to oxidize the gas sample components. The gas flow then passed a volume filled with CuO (oven-heated to 850 ºC) to oxidize any formed CO to CO_2. All formed CO_2 was then cryogenically (liquid N_2) trapped and the rest of the gas (mainly N_2 and O_2) was released at the end of the system. For each sample, the combustion process lasted 2 hr, as (in general) the obtained CO_2 yield was then sufficient (> 250 mL). To obtain pure CO_2 for the measurements, the combusted gas flow first passed different steps to remove water and contaminants like oxidized nitrogen and sulfur components, using heated pure Ag (450 ºC), (acidified) $KMnO_4$ solution, and cryogen (dry ice/ethanol) water traps. Remaining NO_x components in the obtained CO_2-fraction were removed using pure Cu (at 600 ºC). All obtained CO_2 samples were stored in vacuum-pumped 200- or 500-mL cylinders.

3.2.4 ^{13}C and ^{14}C measurement of CO_2 samples

For the isotope measurements a small aliquot (~ 5 mL) of each obtained CO_2 sample from the different biogas and natural gas samples was used. This CO_2 volume was cryogenically trapped in a 20-mL flask. For the ^{14}C measurements of all biogas CO_2 samples, the CO_2 was trapped in 20-mL flasks containing Sulfix (WAKO, 8~20 mesh). This Sulfix removes sulfur-containing compounds when heating the flasks in special ovens (at 200 ºC) during one night. Without this pre-treatment, the graphitization of these CO_2 samples was not possible.

The $\delta^{13}C$ measurements of all CO_2 samples were performed with either a SIRA-10 or OPTIMA IRMS. For the ^{14}C measurement with an AMS system, all CO_2 samples were graphitized to approximately 2 mg graphite and pressed into aluminum targets (Aerts-Bijma et al. 1997). The targets were measured on $^{12,13,14}C$ with the ^{14}C-dedicated AMS (High Voltage Europa Tandetron) of the Centre for Isotope Research laboratory in Groningen (Wijma et al. 1996; van der Plicht et al. 2000).

3.2.5 Bio-fossil CO_2 mixtures

Two different series of bio-fossil CO_2 mixtures were made, with samples ranging between 0 and 100% bioC. In one series, the $\delta^{13}C$ values of the mixed bioC and fossilC were very different. In the other series, the $\delta^{13}C$ values of both fractions were similar. To make a bio-fossil CO_2 mixture, CO_2 samples from both gases were expanded into calibrated volumes, each at specific pressure. Both cryogenically trapped portions were subsequently expanded and mixed in the evacuated system and, together, cryogenically trapped and expanded once more to obtain a homogeneous mixture. The obtained bio-fossil CO_2-mixture was expanded into two 20-mL flasks. One flask contained Sulfix (see above) and was used for the ^{14}C analysis of the mixture, while the other flask was used for the IRMS $\delta^{13}C$ measurement.

3.3 Calculation methods

The calculation of the ^{13}C and ^{14}C values ($\delta^{13}C$ and $^{14}C_{sample\_measured}$) and the general description of the calculation of the ^{14}C-based biogenic carbon fraction as applied to the gas samples of this study are described in chapter 1. This section describes the calculation methods that were used to investigate the isotope fractionation correction and quantify related deviations in the biogenic carbon fraction.

3.3.1 Isotope fractionation correction

As already described in more detail in chapter 1, the amount of ^{14}C in a sample is calculated according to the following equation.

$$^{14}C_{sample\_measured}(\%) = \frac{^{14}A_N^S}{^{14}A_{RN}^0} = \frac{^{14}A^S \cdot \left[\frac{1+\delta^{13}C_N}{1+\delta^{13}C_{sample}}\right]^2}{^{14}A_{RN}^0} \cdot 100\% \qquad (3.1)$$

The term $\left[\frac{1+\delta^{13}C_N}{1+\delta^{13}C_{sample}}\right]^{\phi}$ in this equation corrects the measured ^{14}C amount for isotope fractionation based on ^{13}C isotope ratio measurements to a normalized value, of -0.025 or -25‰ (relative to VPDB), where, by convention, ϕ is 2 (although ϕ is somewhat smaller than 2) as shortly explained in Mook and van der Plicht (1999).

In the normal, routine isotope fractionation correction of an AMS ^{14}C sample, the $\delta^{13}C$ value of the sample ($\delta^{13}C_{sample}$) is used as measured with the AMS ($\delta^{13}C_{sample} = \delta^{13}C_{AMS}$). In this routine correction, $\delta^{13}C_{AMS}$ is measured in the total carbon fraction of the sample. It includes the $\delta^{13}C$ contributions of the different carbon components in the sample and the different fractionation effects ($\alpha^{13}C_X$) during the sampling, pre-treatment and measurement processes of the whole sample. In the case of bio-fossil carbon mixtures, the measured $\delta^{13}C_{AMS}$ value thus also includes the fractionation contribution (with $\alpha^{13}C = \delta^{13}C + 1$) to the ^{14}C-free fossil carbon fraction:

$$\delta^{13}C_{AMS} + 1 = \left(\left(1+\delta^{13}C_{bioC}\right) \cdot fC_{bio} + \underline{\left(1+\delta^{13}C_{fosC}\right) \cdot fC_{fos}} \right) \cdot \alpha^{13}C_X \qquad (3.2)$$

With,

$$\alpha^{13}C_X = \alpha^{13}C_{sampling} \cdot \alpha^{13}C_{pretreatment} \cdot \alpha^{13}C_{AMS\_measurement} \qquad (3.3)$$

For a correct isotope fractionation correction, the fractionation in the ^{13}C signal should be representative for the fractionation in the ^{14}C signal. This is only the case if the abundances of both ^{13}C and ^{14}C have changed (in a constant ratio) during the same chemical and physical processes. In the case of bio-fossil mixtures, the ^{14}C-free fossil carbon has a certain $\delta^{13}C$ value before the mixing with the ^{14}C-containing biogenic carbon. This fossil $\delta^{13}C$ value is not related to any fractionation in the ^{14}C of the mixed bio-fossil sample. Hence, the ^{13}C atoms of the fossil carbon fraction and the ^{14}C atoms of the biogenic fraction have not followed the same fractionation pathways before the mixing of both fractions. The fractionation factor of the fossilC fraction in a sample should therefore be excluded in the fractionation correction. The sample should, in principle, only be corrected based on the $\delta^{13}C$ value that represents the fractionation in the bioC fraction of the sample: $\delta^{13}C_{AMS\_bioC}$

$$\delta^{13}C_{AMS\_bioC} = \left(\left(1+\delta^{13}C_{bioC}\right)\cdot\alpha^{13}C_X\right)-1 \qquad (3.4)$$

If the $\delta^{13}C$ values of the bioC and fossilC fractions are not the same, then the use of the routinely measured $\delta^{13}C_{AMS}$ value instead of $\delta^{13}C_{AMS\_bioC}$ will introduce systematic deviations in the calculation of $^{14}C_{sample\_measured}$ and fC_{bio}. These deviations are likely to occur in mixtures of biogas and natural gas, because these gases show, contrary to many solid and liquid fuels (like wood, coal, ethanol), a wide range of $\delta^{13}C$ values (as explained in the Introduction of this chapter).

The best way to avoid these systematic deviations would be to correct with $\delta^{13}C_{AMS\_bioC}$ instead of $\delta^{13}C_{AMS}$. However, $\delta^{13}C_{AMS\_bioC}$ cannot be measured separately from $\delta^{13}C_{AMS}$ in already mixed bio-fossil samples. Approximation of this value based on the ^{13}C measurement of the bioC fraction of the sample is for most mixtures not possible either. The bioC fraction of bio-fossil mixtures is usually not separately available for measurement on its carbon isotope composition. The use of $\delta^{13}C_{AMS}$ and the related introduction of a deviation in fC_{bio} are therefore inevitable for bio-fossil gas mixtures.

3.3.2 Calculation of the deviation in the bioC fraction

The absolute deviation in the bioC fraction, fC_{bio}, due to the isotope fractionation correction (using $\delta^{13}C_{AMS}$ instead of $\delta^{13}C_{AMS\_bioC}$) was calculated as follows:

$$abs.dev.in\ fC_{bio(\delta^{13}C_{AMS})} = fC_{bio\left(\delta^{13}C_{AMS}\right)} - fC_{bio\left(\delta^{13}C_{AMS\_bioC}\right)} \qquad (\times 100;\ \%) \qquad (3.5)$$

With,

$$fC_{bio\left(\delta^{13}C_{AMS}\right)} = \frac{{}^{14}a^{S}_{(sample\_measured)}}{{}^{14}a^{S}_{N\,(bioC)}} \cdot \left[\frac{0.975}{\left(1+\delta^{13}C_{AMS}\right)}\right]^{2} \tag{3.6}$$

and

$$fC_{bio\left(\delta^{13}C_{AMS\_bioC}\right)} = \frac{{}^{14}a^{S}_{(sample\_measured)}}{{}^{14}a^{S}_{N\,(bioC)}} \cdot \left[\frac{0.975}{\left(1+\delta^{13}C_{AMS\_bioC}\right)}\right]^{2} \tag{3.7}$$

If no fractionation correction is applied at all, the absolute deviation in the biogenic carbon fraction is:

$$abs.\,dev.\,in\ fC_{bio(no\,corr)} = fC_{bio\,(no\,corr)} - fC_{bio\left(\delta^{13}C_{AMS\_bioC}\right)} \tag{3.8}$$

With,

$$fC_{bio\,(no\,corr)} = \frac{{}^{14}a^{S}_{(sample\_measured)}}{{}^{14}a^{S}_{N\,(bioC)}} \tag{3.9}$$

This study calculates the deviations based on real ^{13}C and ^{14}C measurements of bio-fossil mixtures and based on different theoretical cases. When calculating the theoretical cases, the $\delta^{13}C$ value of each theoretical sample (with a certain biogenic carbon fraction between 0 and 100%) was determined based on the chosen $\delta^{13}C$ values of the 100% bioC and 100% fossilC fractions and the chosen bioC fraction of the sample. For these cases, $\delta^{13}C_{AMS}$ is replaced by $\delta^{13}C_{bio-fossil\,sample}$ and $\delta^{13}C_{AMS\_bioC}$ by $\delta^{13}C_{100\%\,bioC}$ in Equations 3.5 - 3.8. To calculate $fC_{bio\left(\delta^{13}C_{AMS\_bioC}\right)}$ (Equation 3.7) for the real measurements, $\delta^{13}C_{AMS\_bioC}$ (Equation 3.4) was approximated as follows, because it could not be measured directly in the mixed bio-fossil samples:

$$\delta^{13}C_{AMS\_bioC} \cong \left(\left(1+\delta^{13}C_{IRMS\_100\%bioC}\right)\cdot\frac{\left(1+\delta^{13}C_{AMS}\right)}{\left(1+\delta^{13}C_{IRMS}\right)}\right)-1 \tag{3.10}$$

With,

$$\delta^{13}C_{IRMS\_100\%bioC} = \left(\left(1+\delta^{13}C_{bioC}\right)\cdot\alpha^{13}C_{sampling\_bioC}\cdot\alpha^{13}C_{pretreatment\_bioC}\right) \quad (3.11)$$

$^{13}\delta_{IRMS\_100\%bioC}$ is the $\delta^{13}C$ value of the separately available and measured bioC material (that was used to make a bio-fossil mixture). It represents the $\delta^{13}C$ value of the bioC material in the mixed bio-fossil sample after sampling, pre-treatment and combustion to CO_2 and

$$\frac{\left(1+\delta^{13}C_{AMS}\right)}{\left(1+\delta^{13}C_{IRMS}\right)} = \alpha^{13}C_{AMS\_measurement} \quad (3.12)$$

Here, $^{13}\alpha_{AMS\_measurement}$ represents the fractionation in each measured bio-fossil mixture after graphitization (which is minimal according to Aerts-Bijma et al. 1997) and AMS measurement. $\delta^{13}C_{IRMS}$ is the $\delta^{13}C$ value of the bio-fossil sample before it is graphitized and $\delta^{13}C_{AMS}$ is the $\delta^{13}C$ value of the sample after graphitization and measurement with AMS.

3.4 Results and discussion

This section first gives an overview of the origin and composition of the different biogas and natural gas samples investigated in this study. The ^{13}C (IRMS) and ^{14}C (AMS) measurement results are given for the separated CO_2 and (combusted) CH_4-fractions of the eight biogas samples and for the measured CO_2 of the three combusted natural gas samples. The measured carbon isotope values are discussed in detail and the results compared with other studies. A new approach is then presented to determine the ^{14}C reference values for different biogas samples. The implications of this approach are considered for the accuracy of the bioC fraction calculation. Next, systematic deviations in the calculated bioC fraction due to departures from the correct isotope fractionation correction are presented and discussed. Finally, examples are given of possible errors in the calculated bioC fraction due to the combination of different error sources.

3.4.1 Origin and composition of the investigated gases

The molecular compositions of the investigated gas samples, as analyzed after sampling and prior to the gas pretreatment procedure, are shown in Table 3.1. The sample names give information about the origin or production source of the gases. All biogas samples come from Dutch production plants. The biogas samples “Landfill_1” and “Landfill_2” are from two different municipal solid waste landfill sites. “Organic waste” is biogas from the digestion of the (wet) organic fraction of municipal waste. “Cookies_fish” is biogas from the waste materials of two different food factories where cookies and fish-products are produced. “Mun. sewage sludge” is biogas from municipal sewage sludge. “Manure_vegetables” has been produced from manure together with grass, maize, vegetable fat and fried potatoes. The biogases Sugar beet and Manure_vegetables are used in Combined Heat and Power stations (CHP). The other biogases are injected into Dutch national distribution gas networks after pretreatment. The exact production sites of the natural gas samples are classified (by DNV KEMA). ‘Norway gas’ is a high-caloric gas (caloric value > 37 MJ/m^3); all other bio- and natural gases are low-caloric gases.

Table 3.1. Main molecular composition (in mol%) of the investigated biogas samples and natural gas samples prior to pretreatment in the laboratory (measurements by DNV KEMA).

Biogas	CH_4 (mol%)	CO_2 (mol%)	C_xH_y (mol%)	(N_2, O_2,..) (mol%)
Maize_onions	56.27	42.20	0.02	1.52
Landfill_1	61.13	32.12	0.00	6.75
Organic waste	61.47	38.35	0.00	0.18
Cookies_fish	85.24	11.96	0.00	2.81
Mun. sewage sludge	89.49	10.25	0.00	0.26
Landfill_2	54.43	30.47	0.00	15.10
Sugar beet	87.75	8.15	0.00	4.07
Manure_vegetables	59.56	35.75	0.00	4.70
Natural gas				
Norway gas	87.10	2.06	8.90	1.95
North Sea gas	85.07	2.66	4.93	7.34
Groningen gas	81.05	1.02	3.45	14.48

3.4.2 ^{13}C and ^{14}C measurement results biogas and natural gas

The results of the ^{13}C and ^{14}C analyses for the combusted biogas-CH_4 fractions and the combusted natural gas samples are listed in Table 3.2. Table 3.3 lists the ^{13}C and ^{14}C analyses results for the CO_2 fraction of the (raw) biogas samples. The $\delta^{13}C$ values (in ‰; with respect to VPDB) and the $^{14}C_{sample\_measured}$ ($^{14}a_N^S$; expressed in pMC) were calculated according to equations 1.7 and 1.4 respectively.

The CO_2-fraction of the Mun. sewage sludge sample were not analyzed by ^{14}C as the (cryogenic) extraction yield of CO_2 from this biogas was too low for ^{14}C analysis. The yield was lower than expected based on the composition of the biogas. This was also the case for the CO_2-yield of the combusted CH_4 fraction of this biogas sample. A clear reason for this has not been found. The combustion of this gas contaminated the combustion system severely. Contamination might also have played a role in the problematic extraction of the CO_2 fraction of this biogas sample (this has however not been investigated further).

Table 3.2. Measured values for $\delta^{13}C$ (IRMS) and $^{14}C_{sample\_measured}$ (AMS) of biogas CH_4 fractions and natural gas samples after combustion to CO_2.

Biogas CH_4 fraction	$\delta^{13}C$ (‰)	$^{14}C_{sample\_measured}$ (pMC)
Maize_onions	-55.58	102.6
Landfill_1	-61.24	104.0
Organic waste	-52.04	104.5
Cookies_fish	-53.64	104.3
Mun. sewage sludge	-28.55	105.1
Landfill_2	-56.25	116.1
Sugar beet	-39.20	102.3
Manure_vegetables	-48.43	103.4
Natural gas		
Norway gas	-39.86	0.18
North Sea gas	-29.81	0.10
Groningen gas	-28.38	0.05

Table 3.3. Measured values for $\delta^{13}C$ (IRMS) and $^{14}C_{sample\_measured}$ (AMS) of the CO_2 fraction of raw biogas samples.

Biogas CO_2 fraction	$\delta^{13}C$ (‰)	$^{14}C_{sample\_measured}$ (pMC)
Maize_onions	26.57	102.3
Landfill_1	14.96	104.2
Organic waste	3.14	104.1
Cookies_fish	30.45	104.2
Mun. sewage sludge	11.72	-
Landfill_2	6.58	115.8
Sugar beet	-5.55	101.8
Manure_vegetables	8.05	102.8

The absolute measurement errors (1σ) are ± 0.03‰ for all $\delta^{13}C$ values (IRMS), ± 0.3-0.5% for the $^{14}C_{sample\_measured}$ values of the biogas samples and ± 0.10% for the $^{14}C_{sample\_measured}$ values of the natural gas samples. By performing multiple combustions for two of the natural gases (Norway gas and Groningen gas) the reproducibility of the applied combustion method was checked. All individual results (for both ^{13}C and ^{14}C) of these multiple series correspond within 2 times the given measurement error. The (average) $^{14}C_{sample\_measured}$ value of the Norway gas is relatively high for a fossil gas that contains in principle no ^{14}C. Although the Norway gas value is still at background level, the possibility of contamination of the samples prior (mixed with biogas?) or during sampling cannot be excluded.

3.4.3 $\delta^{13}C$ *values*

The $\delta^{13}C$ values of the combusted CH_4 fractions (Table 3.2) of seven different biogas samples vary between -39.2‰ and -61.3‰. This is comparable to the results of studies by Laukenmann et al. (2010) and Levin et al. (2003), who showed $\delta^{13}C$ values between -50 and -70‰ for biogas methane from relatively similar digestion processes. The $\delta^{13}C$ value of -28.6‰ for Mun. sewage sludge is relatively high compared to that of the other investigated biogas samples.

The observed variation between the biogas samples is mainly related to the differences in the anaerobic digestion processes of the biogas production plants. The CH_4 in all investigated biogas samples has been produced by anaerobic digestion of the organic input materials by specific microorganisms (like 'methanogens'; for landfill and sewage sludge also other groups are involved). The main biogas CH_4 formation pathways are the production of methane from acetate by acetotrophic methanogens and from CO_2-reduction by hydrogenotrophic methanogens. Methane obtained from acetate fermentation shows less-depleted $\delta^{13}C$ values than methane obtained from CO_2-reduction (Whiticar et al. 1986; Krzycki et al. 1987; Conrad 2005). This might explain the less-negative $\delta^{13}C$ value of municipal sewage sludge CH_4 (Krzycki et al. 1987). Which pathways occur or dominate the digestion process (and the isotope fractionation), depend on the type and number of microorganisms available in the process and on the parameters that influence these microorganisms and their ability to digest the organic material, like the composition of the organic material and the fermentation temperature (Conrad 2005). Methane from landfill gas has been isotopically analysed in many different studies (Bergamaschi et al. 1998, Carbral et al. 2010; Zyakun et al. 2010) and its $\delta^{13}C$ varies between -30‰ and -60‰ and is often < -45‰, comparable to the measured values in this study (-61.3‰ for Landfill_1 and -56.3‰ for Landfill_2). The variation between different landfill gas samples is, beside the variations in production processes, also due to differences in oxidation rate in time and depth.

The investigated CO_2 fractions of the biogas samples show enriched $\delta^{13}C$ values that vary between -5.6‰ for Sugar beet and +30.5‰ for the Cookies_fish biogas sample. The enrichment of the CO_2 is related to the formation process of the depleted CH_4 (Conrad 2005) and has been measured in other studies as well (Rosenfeld and Silverman 1959; Levin et al. 1993; Laukenmann et al. 2010, Zyakun et al. 2010).

The overall $\delta^{13}C$ value of the biogas samples based on the combined CH_4 and CO_2 fractions in these samples $\left(\delta^{13}C_{biogas} \cong \delta^{13}C_{CH_4} \cdot fC_{CH_4} + \delta^{13}C_{CO_2} \cdot fC_{CO_2}\right)$, varies for the investigated biogas samples between -20‰ (Maize_onions) and -43‰ (Cookies_fish). This

is most likely related to the variation in $\delta^{13}C$ values of the different materials ('ingredients') used in the biogas production process (C3- and C4-plants, different production processes of the biomass based materials).

The $\delta^{13}C$ values of the investigated natural gases vary between -28‰ and -40‰. The variation is small compared to the large range of $\delta^{13}C$ values between -25‰ and -80‰ measured in natural gas samples at different sites (Schoell 1980; Milkov 2005). The variation in $\delta^{13}C$ values of natural gas samples is due to the different and very variable formation processes of the gases (Fuex 1977). The measured $\delta^{13}C$ value of the Groningen gas (-28.4‰) is close to the -29.0‰ shown in Hut et al. (1984) for Groningen natural gas sampled at A.F. Tjuchem in the Netherlands.

3.4.4 ^{14}C values of biogas

The $^{14}C_{sample\_measured}$ values of the carbon components (CH_4, CO_2) in biogas are mainly determined by where and when the specific carbon was taken up as atmospheric CO_2 by plant photosynthesis. Over the last 60 year, the $^{14}C_{sample}$ values of atmospheric CO_2, and thus the $^{14}C_{sample}$ values of organic material, have shown large temporal and spatial variations (the maximum value reached in 1964 is ~90 pmC higher than today's atmosphere). Hua et al. (2013) made an overview of (average) atmospheric $^{14}CO_2$ values on a global scale in the period 1950-2010. Fellner and Rechberger (2009) have investigated the variation in $^{14}C_{sample}$ values for the different components in waste and solid recovered fuel (SRF) (like wood, paper, plastics, vegetables). In their study the $^{14}C_{sample}$ values range between 98 and 135 pmC, depending on the type and mixture of organic materials. The $^{14}C_{sample}$ values of seven of the biogas samples investigated in this study (CO_2 and combusted CH_4 fractions), range between 102 and 105 pmC, while one biogas sample (Landfill_2) is considerably higher, at 116 pmC.

Figure 3.1 shows where the $^{14}C_{sample}$ values of the investigated biogas samples (results of the combusted CH_4 fraction), can be found on the timeline of annual average monthly mean atmospheric $^{14}C_{sample\_measured}$ values (average April-October) of CO_2 measured at Dutch monitoring stations Smilde (1987-2003) and Lutjewad (2003-2011). It gives an impression of the average year of atmospheric $^{14}CO_2$ sampling by plants, and thus for the carbon of the organic materials that was used in the production of the investigated biogas. As all investigated biogas samples were produced in the Netherlands, it is assumed that the products originate from plants that have grown in the Netherlands as well. The (rural) Dutch monitoring sites are therefore assumed to be representative for the sites of plant growth.

For biogas sample Sugar beet it was known that it was produced from sugar beets that were grown, harvested and digested in 2011 in the Netherlands. This is confirmed by the data in Figure 3.1 in which the $^{14}C_{sample}$ value of this biogas sample is the same as the average value measured in Dutch atmospheric air in 2011. For the other biogas samples, it is expected that digested vegetables will in general have $^{14}CO_2$ sampling (and harvest) years, which are close to the year of digestion as they are usually not stored for a long time. This seems to be the case for the Maize_onions sample and also for Manure_vegetables, although the latter also matches the atmospheric 2008 value. Manure carbon could have been from earlier years than the digested vegetables. For municipal sewage sludge and digested food products (like cookies), the average $^{14}CO_2$-sampling (and harvest) year deviates a few years from the year of digestion (2011). This can be expected, because the organic material is not directly digested after harvest, but has first been used in other processes during a certain time period. An example of long-term storage (decades) of atmospheric carbon is wood-based material. In the case of biogas this long-term storage can be found in organic material stored and 'digested' at old landfill sites, as the result of Landfill_2 shows (116 pmC; average atmospheric carbon year is 1988). The storage effect of wood-based plants can also to some extent be seen at landfill sites that are still in use (Landfill_1) and in organic waste, which both contain municipal organic waste fractions that have been recently dumped.

In the calculation of $^{14}C_{sample\_measured}$ (eq. 1.4) the year of harvest of the biogenic organic material, t_S, is needed as well if the decay correction needs to be applied. If biogas or bio-fossil gas mixtures need to be verified and the average harvest year is not known, then the year of digestion should be used instead. Fortunately, this decay correction term varies very little per year and the calculated $^{14}C_{sample\_measured}$ deviates only 0.01% (relatively) with every year of difference between the year of digestion and the average harvest year. For the investigated biogas samples of this study with unknown harvest year the year of digestion: 2011, was used for t_S. For the Sugar beet samples it was known that the harvest year was 2011. If the harvest years for the "unknown" samples are estimated based on Figure 3.1, the use of 2011 instead of the "real" harvest year gives deviations of <0.05 pmC for most of the biogas samples. Only for Landfill_2, for which harvest year (or "average year of growth") 1988 seems to be a good estimate, $^{14}C_{sample\_measured}$ would increase distinctively by 0.3 pmC (from 116.1 to 116.4 pmC) if 1988 had been used for t_s instead of 2011.

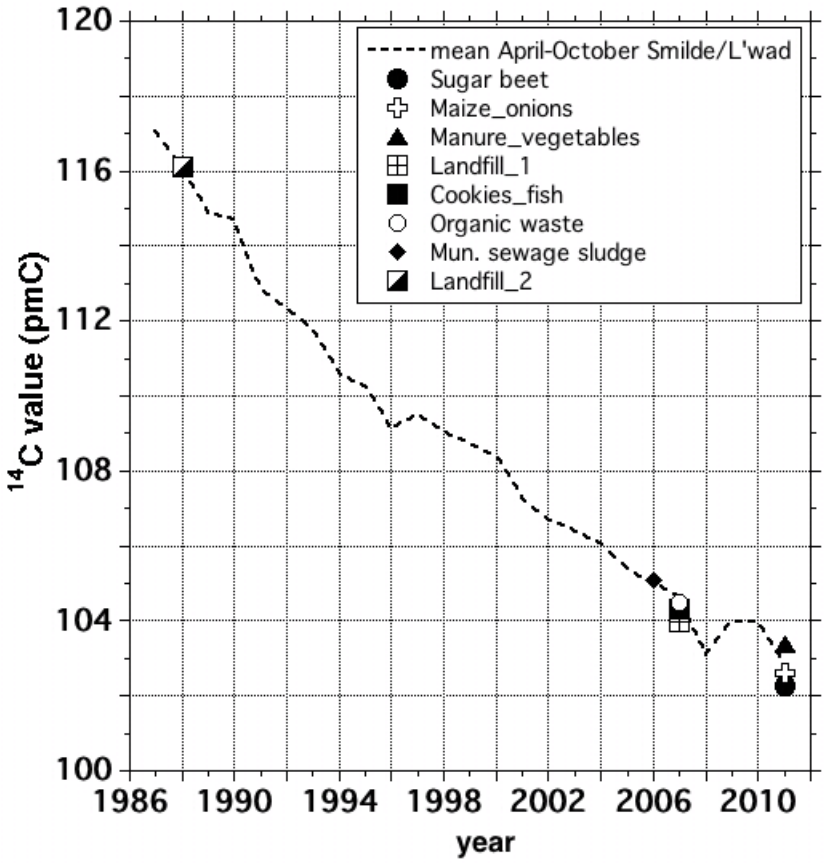

Figure 3.1. Comparison between $^{14}C_{sample\_measured}$ values (pmC) of different biogas samples and average atmospheric $^{14}C_{sample\_measured}$ values (pmC) for the period 1987-2011. The atmospheric $^{14}CO_2$ values have been measured at Dutch monitoring stations Smilde (1987-2002; published before in Meijer et al. 1994 and Palstra et al. 2008) and Lutjewad (2004-2011) by the University of Groningen. The biogas results are from combusted CH_4-fractions. The plotted annual atmospheric $^{14}C_{sample\_measured}$ values are average values from monthly mean $^{14}CO_2$ values of the months April – October. The period in which plants take up atmospheric CO_2 is typically within this period.

The $^{14}C_{sample\_measured}$ values of the separately measured CO_2-fraction and combusted CH_4-fraction of biogas samples agree for all investigated biogas samples within two times the measurement error. This is also expected, as both fractions originate from the same digested organic materials. In cases of fraud-investigation to identify whether biomethane is 100% biogenic, the measurement of the CO_2 fraction could therefore act as an internal reference (comparison with the $^{14}C_{sample\_measured}$ value of the combusted CH_4 fraction).

The observed differences in $^{14}C_{sample\_measured}$ values between both carbon fractions in this study (0.2-0.6 pmC) can be due to other factors than the random measurement errors. For example, variation in the CO_2/CH_4 ratio (mol %) between digested organic materials with different $^{14}C_{sample\_measured}$ values (within the same biogas batch) give different average $^{14}C_{sample\_measured}$ values of CO_2 and CH_4 in a particular biogas sample. Another factor could be the used isotope fractionation ratio of 2 (the factor ϕ in equation 3.1) in the correction of the measured ^{14}C amounts for isotope fractionation. This ratio shows the rate of isotope fractionation of the ^{14}C atoms compared to the ^{13}C atoms in the sample material and is for most processes below 2 (around 1.9). This value varies between different chemical/physical processes due differences in the kinetic and equilibrium reactions in these processes (Mook, 2000), but is impossible to determine for each sample material individually. For most ^{14}C applications the standardized correction factor of 2 instead of the true value is a good approximation and no anomalies will be visible in the final results. If the difference of the $\delta^{13}C$ value of a certain carbon component with the normalized $\delta^{13}C$ value (-25 ‰) is relatively large and the difference in $\delta^{13}C$ value between this carbon component and another carbon component in the same sample material is even larger, which is the case for the CO_2 and CH_4 fractions of raw biogases, then the use of the standardized isotope fractionation rate factor instead of the real factor will introduce slight differences between the $^{14}C_{sample\_measured}$ values of the separate components.

3.4.5 ^{14}C reference value for 100% biogenic carbon

When determining the bioC fraction of biogas and bio-fossil gas mixtures (Eq. 1.3), a ^{14}C reference value for 100% biogenic carbon is needed ($^{14}C_{bio}$). Ideally, this value would be the measured ^{14}C value of the pure biogenic gas that lies at the basis of the sample. Usually, however, this measurement is not possible or feasible, as in most cases the bio-fossil carbon samples are already mixed (and/or combusted). For biogas samples that need to be verified on bioC composition, a $^{14}C_{bio}$ value should be available beforehand and cannot be determined based on the measurement of the biogas sample itself. Therefore, in most cases an approximated value needs to be used that is based on $^{14}C_{sample}$ values of different biogenic materials or based on atmospheric $^{14}CO_2$. An approximated $^{14}C_{bio}$ value will, obviously, introduce a bigger uncertainty in the calculated bioC fraction (fC_{bio}) than a directly measured one. Especially for fraud investigation, where fraud should be significantly identified from systematic and random uncertainties in the determined bioC fraction, it is of interest that the approximated value is reliable and that the uncertainty in this value is as small as possible. Quantification of uncertainties in the calculated bioC fraction, including the uncertainty in the used $^{14}C_{bio}$ value, is therefore essential. So far, however, it has not been part of the procedures of the several (inter)-national standards

in which the ^{14}C method is used to determine the bioC fraction (like ASTM D6866-12 [ASTM 2012] and ISO/FDIS 13833 [ISO 2012]).

This study proposes a method to approximate $^{14}C_{bio}$ values for different types of biogases based on atmospheric $^{14}CO_2$ values. Biogases were divided into four different groups with different (maximum) time periods between growth/harvest and digestion. For each group the $^{14}C_{bio}$ value is calculated based on atmospheric $^{14}CO_2$ values that have been measured in the defined time period of that group. The defined groups are summarized in Table 3.4.

The (average) year of plant growth is known only for group 1. For the other groups this is not known and thus has been estimated based on information about the used organic materials: Group 2 is organic material with atmospheric carbon from the harvest year only, digested within 2 years after harvest. Group 3 consists of two subgroups of organic materials. The first subgroup is organic material with atmospheric carbon from the harvest year only, but which has been pre-treated first before becoming a waste product. The second subgroup is organic material stored in plants for a short average time period (few years). Both subgroups are characterized by an average of up to 5-yr difference in time between harvest and digestion of the material. Group 4 is the most complicated one. It contains mixtures of organic material, stored for a long time period (up to several decades) until digestion to biogas (municipal waste is a typical example). The method proposed here can also be used for other (solid, liquid) bio-fuels. Instead of the year of digestion, the year of bio-fuel production can then be used.

Table 3.5 shows $^{14}C_{bio}$ values for biogases digested in 2011, which was calculated according to the approach of Table 3.4. For groups 1-3 values were calculated based on averaged monthly mean atmospheric $^{14}CO_2$ values measured at Dutch monitoring stations Smilde (2001-2003) and Lutjewad (2004-2011) (Centre for Isotope Research, University of Groningen; monthly mean values of both stations have not been published yet). For each group the average $^{14}C_{sample}$ value was calculated based on monthly data from the period April-October for the year(s) in the given time period of the specific group. The uncertainties given are the standard deviations in the averaged monthly mean values. The (rounded off) $^{14}C_{bio}$ value and its overall uncertainty for biogas group 4 was based on (waste) data by Fellner and Rechberger (2009; see their Table 5).

Table 3.4. Approach to approximate $^{14}C_{bio}$ for different biogas groups.

Biogas group	Approach
1. (Average) year of plant growth is known	Average atmospheric $^{14}CO_2$ value April-October of the (average) year of plant growth
2. Year of plant growth is not known and is expected to differ <2 yr with year of digestion (vegetables, annual grown plants; no wood)	Average atmospheric $^{14}CO_2$ value April-October of the year of digestion and the previous year.
3. (Average) year of plant growth is not known and average difference between biomass harvest and digestion is estimated to be < 10 yr (food residue, manure, sewage sludge, wet organic municipal waste fraction; wood < 10 yr)	Average atmospheric $^{14}CO_2$ values April-October of 10 yr incl. year of digestion.
4. (Average) year of plant growth is not known and average difference between biomass harvest and digestion > 10 yr (municipal waste stored in old landfills, wood > 10 yr).	Average $^{14}C_{sample}$ value of waste materials in year of sampling, based on study by Fellner and Rechberger (2009).

The values in Table 3.5 are valid for 2011 only. Due to the (long-term) annually decreasing $^{14}C_{sample}$ of atmospheric CO_2 (since the 1960s) the approximated $^{14}C_{bio}$ values of the different groups will decrease annually as well (only one-year average values of successive years can show an increase sometimes, as can be seen in fig. 3.1). This long-term decrease is currently approximately -0.5 pmC per year (also for waste according to Fellner and Rechberger 2009). Biogas samples digested in 2012 might therefore have slightly lower $^{14}C_{bio}$ values than those mentioned in table 3.5.

Table 3.5. Approximated $^{14}C_{bio}$ values for (Dutch) biogas samples digested and/or sampled in 2011.

Biogas group	Time period	$^{14}C_{bio}$ (pmC)	± (1σ)
1	2011	102.8	0.5
2	2010-2011	103.4	0.7
3	2001 - 2011	105.0	1.6
4	Not defined (wood materials >1900 AD)	115	4

As the values of group 1-3 in Table 3.5 were calculated based on atmospheric $^{14}CO_2$ values measured in the Netherlands, they represent $^{14}C_{bio}$ values that can be found in organic carbon from plant materials that have grown in the Netherlands. For digested organic materials that have grown in other regions/countries the $^{14}C_{bio}$ values of these organic materials can be different compared to the Dutch materials, as the $^{14}C_{sample}$ values of atmospheric $^{14}CO_2$ and therefore of plant materials as well show spatial variation (Meijer et al. 1995, Levin et al. 2003, Hsueh et al. 2007, Palstra et al. 2008). The $^{14}C_{bio}$ values based on average $^{14}C_{sample}$ values of atmospheric $^{14}CO_2$ could therefore be slightly different as well, if based on atmospheric values of other regions. Investigation of the differences between averaged $^{14}C_{sample}$ values of the Dutch monitoring stations and remote Alpine monitoring station 'Jungfraujoch' and highly urbanized regions (Meijer et al. 1995, Levin et al., 2003, Levin and Kromer 2004, Palstra et al. 2008, data 'Jungfraujoch' >2003 from personal communication with I. Levin, IUP Heidelberg), showed, however, that the Dutch data are in between the values from (European) remote and highly urbanized regions (± 1.5 pmC). The approximated $^{14}C_{bio}$ values in Table 3.5 are therefore useful average values for biogas samples, regardless its organic carbon origin (at least in Europe). Only the shown uncertainties in Table 3.5 will be slightly larger for biogas groups 1–3 due to this spatial variation (with 1σ approximately ± 0.5 pmC). The total (1σ) uncertainties in the approximated $^{14}C_{bio}$ values of biogas groups 1–3 are then ±0.7 pmC, ±0.9 pmC and ± 1.7 pmC respectively, instead of the uncertainties shown in table 3.5.

It was verified whether the $^{14}C_{bio}$ of Table 3.5 give the correct bioC fractions for the investigated biogas samples (Table 3.2), within the given uncertainty ranges. For this verification, it was assumed that all investigated biogas samples contained 100% biogenic carbon. As the investigated biogas samples in this study contain organic carbon from plants materials that have mainly grown in the Netherlands, the values and the given uncertainties in Table 3.5 are expected to be very representative for the investigated biogas samples. The biogas samples have been divided over the four defined groups based on the available information about the organic material used in the biogas production.

Table 3.6 shows the calculated bioC fractions of the biogas samples. The 1σ error in the calculated bioC fraction is determined by the (AMS) measurement error in $^{14}C_{sample\_measured}$ (0.4 pmC for all samples) and by the uncertainty in the approximated $^{14}C_{bio}$ value.

Table 3.6. BioC fraction (fC_{bio}) of the investigated biogas samples using the data of table 3.4 and the classification of table 3.5.

Biogas	Group nr	fC_{bio} (%)	± (1σ)	Deviation with 100% bioC
Sugar beet	1	99.5	0.6	-0.5
Maize_onions	2	99.2	0.8	-0.8
Manure_vegetables	2	100.0	0.8	0.0
Landfill_1	3	99.0	1.6	-1.0
Cookies_fish	3	99.4	1.6	-0.6
Organic waste	3	99.5	1.6	-0.5
Mun. sewage sludge	3	100.1	1.6	0.1
Landfill_2	4	101.0	3.5	1.0

The approach employed to approximate the $^{14}C_{bio}$ value for different groups of biogases works very well for the biogases investigated in this study. All biogas samples contain 100% bioC within 1σ uncertainty and within ± 1%. Dividing the different biogas samples into groups with different approximated $^{14}C_{bio}$ values improves the accuracy of the ^{14}C-method for the different types of biogas samples. The more information available about the average harvest year and the location and time-period of atmospheric carbon uptake, the smaller the uncertainty and systematic deviation in the determined bioC fraction.

Biogas from vegetables that have grown in greenhouses where fossil CO_2 has been added to the air, form a special class of “bio material”. The ^{14}C values of these plants can in principle be much lower than atmospheric $^{14}CO_2$ values due to the dilution with ^{14}C-free fossil carbon. If the bioC fraction of these (pure) biogases is calculated using a 100% bioC reference value as determined according to the method described in Table 3.4, this bioC fraction will be lower than 100%. On the one hand, this is not satisfactory since the formed gas is purely “biogenic”, that is, recently formed by photosynthesis. On the other, the ^{14}C method correctly shows that fossil fuel CO_2 is involved, and is right in the sense that using this biogas will only partially prevent the emission of fossil fuel CO_2 into the atmosphere. What is desirable in this application of the ^{14}C method for biogas samples is a matter of definition, but both practical and principal arguments are in favor of the correctness of the ^{14}C-based determination.

3.4.6 Deviations in the bioC fraction related to isotope fractionation correction

This section presents deviations in the bioC fraction due to incorrect isotope fractionation correction. Results are given for two experimental and five theoretical cases in which ^{14}C measurement results have been corrected based on $\delta^{13}C_{AMS}$ instead of $\delta^{13}C_{AMS\_bioC}$ for the experimental cases and based on $\delta^{13}C_{bio-fossil\ sample}$ instead of $\delta^{13}C_{100\%\ bioC}$ for the theoretical cases. The experimental cases are based on real ^{13}C and ^{14}C measurements of two different mixture series of biogenic and fossil CO_2 (both from combusted CH_4 samples). Deviations were calculated according to Equation 3.5 for the theoretical cases and according to Equation 3.5 combined with Equation 3.10 (approximated value for $\delta^{13}C_{AMS\_bioC}$) for the experimental cases. Another two theoretical cases, in which no isotope fractionation correction has been applied, have been investigated as well (using Equation 3.8). The $\delta^{13}C$ values of the separate bioC and fossilC fractions and the $^{14}C_{bio}$ values that have been used to investigate theoretical bio-fossil mixtures are summarized in Table 3.7.

For the two experimental cases, the measured $\delta^{13}C$ and (uncorrected for fractionation) measured ^{14}C results (calculated as $^{14}a^{S}$ value, reported in pMC) of different bio-fossil samples (with bioC fractions ranging between 0 and 100%) are shown in Tables 3.8 and 3.9. The chosen values for theoretical cases 1 and 2 (Table 3.7) are identical to the values of the experimental cases 1 and 2 respectively.

Figure 3.2 shows the absolute deviations in the calculated bioC fractions for the different investigated experimental and theoretical cases.

Table 3.7. $\delta^{13}C$ values of bioC and fossilC fractions and $^{14}C_{bio}$ values, used to calculate deviations in different bioC fractions of theoretical bio-fossil carbon mixtures.

	$\delta^{13}C_{100\%\ fossilC}$ (‰)	$\delta^{13}C_{100\%\ bioC}$ (‰)	$^{14}C_{bio}$ (pmC)
Theor. & no corr. case 1	-28.38	-61.24	104.0
Theor. & no corr. case 2	-39.86	-39.20	102.3
Theor. case 3	-50.00	-30.00	100.0
Theor. case 4	-30.00	-40.00	100.0
Theor. case 5	-25.00	-75.00	100.0

Table 3.8. Measured $\delta^{13}C$ and $^{14}a^{S}$ values of experimental case 1: CO_2 mixtures of combusted Landfill_1 biogas ($\delta^{13}C_{IRMS}$ = -61.24‰ and $^{14}C_{bio}$ =104.0 pmC) and combusted Groningen natural gas ($\delta^{13}C_{IRMS}$ = -28.38‰). Samples 1 and 11 show the values for the 100% fossilC sample and 100% bioC sample, respectively.

	$^{14}a^{S}$ (pMC)	±	$\delta^{13}C_{IRMS}$ (‰)	$\delta^{13}C_{AMS}$ (‰)
1 (0% bioC)	0.05	0.04	-28.38	-28.8
2	2.80	0.05	-29.19	-28.0
3	5.50	0.07	-30.12	-31.7
4	6.40	0.08	-30.42	-28.2
5	22.7	0.1	-36.57	-36.4
6	45.8	0.2	-43.98	-45.6
7	64.5	0.3	-49.94	-50.2
8	70.1	0.3	-52.59	-50.1
9	90.7	0.4	-59.28	-59.2
10	95.6	0.4	-61.03	-60.0
11 (100% bioC)	96.1	0.5	-61.24	-62.6

Table 3.9. Measured $\delta^{13}C$ and $^{14}a^{S}$ values of experimental case 2: CO_2 mixtures of combusted Sugar_beet biogas ($\delta^{13}C_{IRMS}$ = -39.20‰ and $^{14}C_{bio}$= 102.3 pmC) and combusted Norway natural gas ($\delta^{13}C_{IRMS}$ = -39.86‰). Samples 1 and 12 show the values for the 100% fossilC sample and 100% bioC sample, respectively.

	$^{14}a^{S}$ (pMC)	±	$\delta^{13}C_{IRMS}$ (‰)	$\delta^{13}C_{AMS}$ (‰)
1 (0% bioC)	0.16	0.06	-39.86	-40.1
2	1.72	0.05	-39.80	-39.4
3	6.40	0.08	-39.51	-40.7
4	28.5	0.2	-39.62	-41.0
5	31.2	0.2	-39.63	-37.6
6	32.1	0.2	-39.60	-39.1
7	46.5	0.2	-39.48	-40.8
8	69.3	0.3	-39.41	-39.6
9	91.6	0.4	-39.42	-38.7
10	93.5	0.4	-39.26	-38.7
11	95.3	0.4	-39.13	-39.8
12 (100% bioC)	98.9	0.5	-39.20	-40.7

Isotope fractionation correction based on the $\delta^{13}C$ value of bio-fossil mixtures, instead of the $\delta^{13}C$ value of the bioC fraction alone, results in systematic deviations when calculating the bioC fraction of a sample. These deviations increase with increasing difference between $\delta^{13}C_{bioC}$ and $\delta^{13}C_{fossilC}$, and are maximal for samples with 50% bioC. The calculated bioC fraction decreases due to this deviation if $\delta^{13}C_{bioC} < \delta^{13}C_{fossilC}$ and increases if $\delta^{13}C_{bioC} > \delta^{13}C_{fossilC}$. There is no deviation in the calculated bioC fraction if $\delta^{13}C_{bioC} = \delta^{13}C_{fossilC}$, as is also shown by experimental case 2 and theoretical case 2. As the $\delta^{13}C$ values of biogas and natural gas can vary considerably, but will in general not differ more than 50‰ (theor. case 5), absolute deviations in a calculated bioC fraction between 0 and ± 2.5% can be expected for bio-fossil gas mixtures with unknown $\delta^{13}C$ values of the bioC and fossilC fractions.

If no isotope fractionation correction is applied (published LSC measurements are often not corrected for isotope fractionation and the application of the correction is often questioned by users of LSC-based ^{14}C-data), the systematic deviation in the calculated bioC fraction increases with increasing difference between the $\delta^{13}C_{bioC}$ value of the investigated sample and $\delta^{13}C_N$ (the normalized $\delta^{13}C$ value of -25‰). The absolute deviation increases with increasing bioC fraction, is maximal at 100% bioC and can be up to -10% for biogases. Especially if biogas samples are verified for their bioC content (verification of 100% bioC), no fractionation correction of the measured ^{14}C value in the sample will give erroneous verification results.

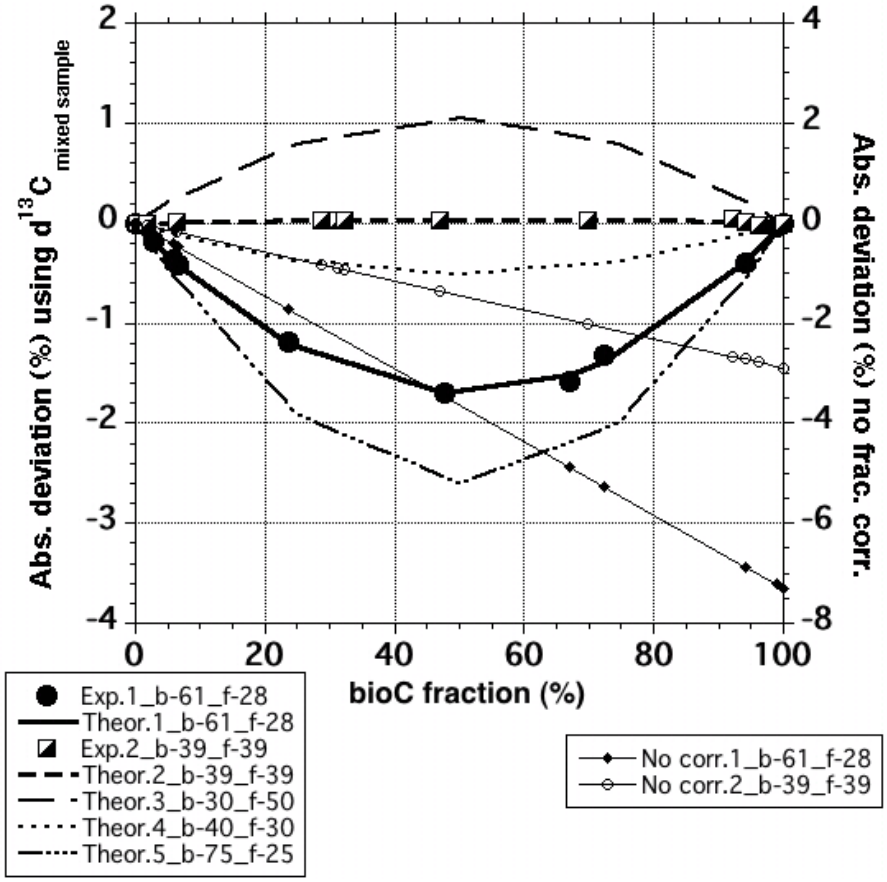

Figure 3.2. Absolute deviations in the calculated bioC fraction (%) for two experimental (exp.) and five theoretical cases (theor.) in which the measured ^{14}C value has been corrected for isotope fractionation based on the $\delta^{13}C$ value of the bio-fossil sample instead of the $\delta^{13}C$ value of the bioC fraction in the sample alone. The figure also shows the absolute deviation in the bioC fraction for two cases in which no isotope fractionation correction has been applied at all (no corr.; mind the different y-axis scale). In the figure text, 'b-61_f-28' means a $\delta^{13}C$ value of -61‰ for the bioC fraction and $\delta^{13}C$ value of -28‰ for the fossilC fraction.

3.4.7 Accuracy of the ^{14}C method for biogas/natural gas fuel mixtures

In the previous sections, two principle sources of error in the calculated bioC fraction have been demonstrated for bio-fossil gas mixtures: the uncertainty in the $^{14}C_{bio}$ value and deviations due to isotope fractionation correction. These error sources are part of the ^{14}C method to determine the bioC fraction, irrespective of the ^{14}C measurement technique used or the investigated bio-fossil carbon material. The quantity of the possible errors, however, depends on these latter factors as well. Results are presented that have been measured with AMS, which has, compared to LSC ^{14}C measurements (Norton and Devlin, 2006), a relatively low measurement uncertainty. Reported uncertainties in calculated bioC fractions based on AMS ^{14}C measurements are therefore more accurate and are not representative for the results based on LSC measurements. The accuracy of the ^{14}C method varies between the different ^{14}C measurement techniques. This should be taken into account in the use of this application for verification purposes.

Figure 3.3 gives an overview (theoretical cases) of possible errors in the calculated bioC fraction for two groups of bio-fossil gas mixtures, if measured with AMS, using an approximated reference value for 100% bioC and with unknown $\delta^{13}C$ values of the separate bio-fossil fractions. Table 3.4 defines different biogas groups. Each group has a certain uncertainty in $^{14}C_{bio}$. Group 1, biogases with known harvest year, has the lowest uncertainty and group 4, landfill biogas, has the highest uncertainty. In Figure 3.3, the results of both groups together show the range of possible errors in the ^{14}C-based method to calculate bioC fractions for bio-fossil gas mixtures. The possible errors given for groups 1 and 4 are a combination of the (1σ) uncertainties in the ^{14}C measurement and in the approximated $^{14}C_{bio}$ value and the uncertainty in the size of the deviation due to possible incorrect isotope fractionation.

The case 'Measurement uncertainty' ('meas. uncer.' in the graph) shows the 1σ range of the random variation in the calculated bioC fraction due to the AMS measurement uncertainty alone. The values $^{14}C_{sample}$ and $^{14}C_{bio}$ in the calculation of the bioC fraction (eq. 1.3) are in this case both directly measured with AMS. The error increases with increasing bioC fraction and is in our study maximal 0.7%. This is the minimal (1σ) error in calculated bioC fractions as determined with the ^{14}C method.

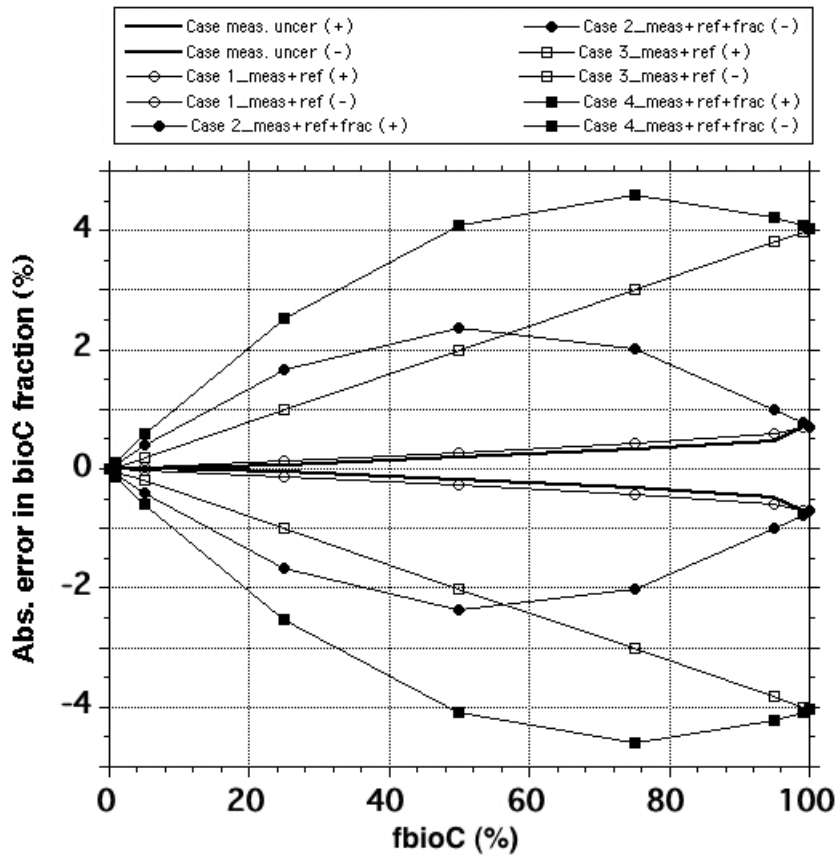

Figure 3.3. Ranges of possible (±) errors in the calculated bioC fraction (%), which are typical for specific biogas and bio-fossil gas mixtures if measured with AMS. Cases 1 and 2 represent bio-fossil gas mixtures with biogas from group 1 (as defined in Table 3.4). Cases 3 and 4 represent mixtures with biogas from group 4. In the figure text: "meas" is 'measurement uncertainty', "ref" is the uncertainty in the estimated 100% bioC reference value, and "frac" is the the systematic error in the isotope fractionation correction.

Cases 1 and 2 show the results for biogases of group 1 and cases 3 and 4 represent wood-based and landfill biogases (group 4). In these cases, the uncertainty in the approximated $^{14}C_{bio}$ values is ± 0.5 pmC for cases 1 and 2 and ± 4 pmC for cases 3 and 4 (using Table 3.5). The possible deviation in the calculated bioC fraction due to incorrect isotope fractionation (if the $\delta^{13}C$ values of the separate bioC and fossilC fractions in the sample are unknown) varies between 0 ($\delta^{13}C_{bioC} = \delta^{13}C_{fossilC}$; cases 1 and 3) and a certain expected maximum value that depends on the possible difference between $\delta^{13}C_{bioC}$ and $\delta^{13}C_{fossilC}$ for the investigated type of sample material ($\delta^{13}C_{bioC} \neq \delta^{13}C_{fossilC}$; cases 2 and 4). The differences in $\delta^{13}C$ values between the biogenic and fossil gases investigated in this

study range from +10 and -33‰. Differences up to 50‰ may be possible, but these differences will not occur often. Differences up to +40‰ and -40‰ are more likely and these both values have therefore been used in the calculation of the uncertainty range for cases 2 and 4. Cases 1 and 3 represent the minimal uncertainty in the calculated bioC fraction for bio-fossil gas mixtures for groups 1 and 4, respectively. For biogases with harvest years < 2 yr or < 10 yr before digestion (in Table 3.4: groups 2 and 3, respectively), the results are in between those of groups 1 and 4. Cases, for which no isotope fractionation correction has been applied, are not shown in this figure (and would show larger deviations, see fig. 3.2).

For verification whether biogases (especially its methane fraction) contain 100% bioC, the 100% bioC fraction can be determined with an (1σ) uncertainty of ± 0.7%, ± 0.9%, ± 1.7 and ± 4% for the biogas groups 1, 2, 3 and 4, respectively (Table 3.4).

For bio-fossil gas mixtures, the (partly 1σ) errors in the calculated bioC fractions can be up to ± 2.5% (at bioC of 50%), ± 2.5% (at 55% bioC), ± 3.0% (at 60% bioC) and ± 4.5% (at 75% bioC) for the biogas groups 1, 2, 3 and 4, respectively.

3.5 Conclusions and recommendations

This study measured the ^{13}C ($\delta^{13}C$) values and $^{14}C_{sample\_measured}$ values of eight different biogas samples, three different natural gas samples and several bio-fossil gas mixtures with IRMS and AMS. The measured $\delta^{13}C$ values varied between -6 and +31‰ for the CO_2 fractions of the biogases, between -28 and -62‰ for the combusted CH_4 fractions of the biogases and between -28 and -40‰ for the combusted natural gases. ^{14}C values of the investigated biogases varied between 102 and 116 pmC and were <0.2 pmC for natural gases.

A method is proposed to minimize the uncertainty in the calculated bioC fraction of a biogas or bio-fossil gas mixture, by dividing biogases into 4 different groups with different uncertainty ranges. This method can be used for other bio-fuels as well and we recommend its adoption in several (international) standards. The uncertainty in the calculated bioC fraction due to the uncertainty in the approximated $^{14}C_{bio}$ value varies between ± 0.5% and ± 3.5% for the different defined biogas groups.

Systematic deviations arise in the calculated bioC fractions if in the isotope fractionation correction the $\delta^{13}C$ value of the mixed bio-fossil sample is used instead of the $\delta^{13}C$ value of the bioC fraction alone. The size of this deviation increases with increasing difference between the $\delta^{13}C$ values of the bioC and fossilC fractions in the sample. For bio-fossil gas mixtures, differences can be up to 50‰ and deviations in the calculated bioC fraction of up to ± 2.5% (at 50% bioC fraction) are therefore possible. If no isotope fractionation correction is applied in the calculation of the bioC fraction for biogases and bio-fossil gas mixtures, the absolute error in the determined bioC fraction can be up to -8%.

The possible errors in the determined bioC fractions were determined for the four biogas groups (Table 3.4). These values represent samples measured with AMS, for which an approximated $^{14}Cbio$ value is used and the $\delta^{13}C$ values of the separate bio-fossil fractions are unknown.

For 100% bioC-verification of biogases (biomethane), the 100% bioC fraction can be determined with an (1σ) uncertainty of ± 0.7%, ± 0.9%, ± 1.7 and ± 4% for the different defined biogas groups 1, 2, 3 and 4, respectively.

For bio-fossil gas mixtures, the errors in the calculated bioC fractions can be up to ± 2.5% (at bioC of 50%), ± 2.5% (at 55% bioC), ± 3.0% (at 60% bioC) and ± 4.5% (at 75% bioC) for the biogas groups 1, 2, 3 and 4, respectively.

Knowledge about the origin and composition of the organic material used in the production of biogas is essential to minimize the uncertainties in the ^{14}C-based determination of the bioC fraction of biogas samples and bio-fossil gas mixtures.

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